

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> C08F 226/06, 220/60, 220/04 C08F 220/34	<b>A1</b>	<b>(11) International Publication Number:</b> WO 93/25595 <b>(43) International Publication Date:</b> 23 December 1993 (23.12.93)																																				
<b>(21) International Application Number:</b> PCT/US93/04823 <b>(22) International Filing Date:</b> 20 May 1993 (20.05.93)  <b>(30) Priority data:</b> 899,965 17 June 1992 (17.06.92) US 906,163 29 June 1992 (29.06.92) US  <b>(71) Applicant:</b> ISP INVESTMENTS INC. [US/US]; 818 Washington Street, Wilmington, DE 19801 (US). <b>(72) Inventor:</b> SHIH, Jenn, S. ; 255 Washington Place, Paramus, NJ 07652 (US). <b>(74) Agents:</b> MAUE, Marilyn, J. et al.; International Specialty Products, 1361 Alps Road, Wayne, NJ 07470 (US).		<b>(81) Designated States:</b> JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>																																				
<b>(54) Title:</b> CATIONIC POLYMER COMPOSITIONS  <div data-bbox="500 1178 1187 1675"><table border="1"><caption>Data points estimated from the graph</caption><thead><tr><th>% Crosslinker</th><th>Gel Volume (ml/g)</th><th>Brookfield Viscosity (Thousands, cps)</th></tr></thead><tbody><tr><td>0.0</td><td>0</td><td>0</td></tr><tr><td>0.1</td><td>100</td><td>55</td></tr><tr><td>0.2</td><td>280</td><td>55</td></tr><tr><td>0.3</td><td>240</td><td>45</td></tr><tr><td>0.4</td><td>200</td><td>35</td></tr><tr><td>0.5</td><td>160</td><td>25</td></tr><tr><td>0.6</td><td>120</td><td>15</td></tr><tr><td>0.7</td><td>80</td><td>10</td></tr><tr><td>0.8</td><td>60</td><td>5</td></tr><tr><td>0.9</td><td>40</td><td>2</td></tr><tr><td>1.0</td><td>20</td><td>0</td></tr></tbody></table></div> <b>(57) Abstract</b> <p>What is provided herein are cationic polymer compositions comprising a cationic polymer of strongly swellable, moderately cross-linked vinyl lactam, e.g. vinylpyrrolidone, and a quaternized amino alkyl acrylamido or acrylate, e.g. quaternized dimethylaminopropyl methacrylamide or dimethylaminoethyl methacrylate, optionally including a polymerizable carboxylic acid, e.g. acrylic acid or methacrylic acid, which includes about 0.1-0.8 % of a cross-linking agent therein. These polymer compositions, in a concentration of 1-10 % by weight in aqueous and non-aqueous medium, provide effective thickener action while imparting cationic characteristics to the resulting solution.</p>			% Crosslinker	Gel Volume (ml/g)	Brookfield Viscosity (Thousands, cps)	0.0	0	0	0.1	100	55	0.2	280	55	0.3	240	45	0.4	200	35	0.5	160	25	0.6	120	15	0.7	80	10	0.8	60	5	0.9	40	2	1.0	20	0
% Crosslinker	Gel Volume (ml/g)	Brookfield Viscosity (Thousands, cps)																																				
0.0	0	0																																				
0.1	100	55																																				
0.2	280	55																																				
0.3	240	45																																				
0.4	200	35																																				
0.5	160	25																																				
0.6	120	15																																				
0.7	80	10																																				
0.8	60	5																																				
0.9	40	2																																				
1.0	20	0																																				

**FOR THE PURPOSES OF INFORMATION ONLY**

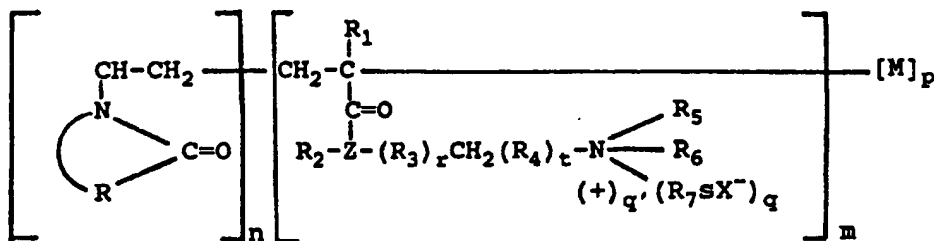
Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

CATIONIC POLYMER COMPOSITIONS

The cationic polymer of the invention comprises 50-99 mole % of a strongly swellable, moderately crosslinked vinyl lactam, e.g. vinylpyrrolidone, and 1-50 mole % of a quaternized amino alkyl acrylamide, e.g. quaternized dimethylaminopropyl methacrylamide, and including about 0.1-0.8% of a crosslinking agent. Compositions of these cationic polymers effectively thicken both aqueous and non-aqueous solutions at a concentration of 1-10% by weight of the polymer while imparting cationic characteristics to the resulting product.

The cationic (quaternized) polymer product has the formula:



where R is alkylene having from 3 to 8 carbon atoms optionally substituted with lower alkyl; R<sub>1</sub> and R<sub>2</sub> are each independently hydrogen or methyl; R<sub>3</sub> and R<sub>4</sub> are each alkylene having from 1 to 18 carbon atoms optionally substituted with alkyl; the sum of r and t is one or zero; R<sub>5</sub> and R<sub>6</sub> are each independently lower alkyl; Z is oxygen or nitrogen; if oxygen, R<sub>2</sub> is absent; M is a polymerizable carboxylic acid; n has a value of from 1 to 99 mole %; m has a value of from 1 to 99 mole %; p has a

- 2 -

value of from 0 to 98 mole %; the sum of  $m + n + p$  is 100; preferably,  $n$  is 50 to 90 mole %;  $m$  is 7 to 25 mole % and  $p$  3 to 25 mole %;  $R_7sX^-$  is a quaternizing group, in which  $R_7$  is lower alkyl, pyrrolidonyl alkyl, carboxymethylene, or a zwitterion of  $\beta$ -propiolactone;  $X$  is an anion derived from the group of halogen,  $SO_3$ ,  $SO_4$ ,  $HSO_4$  and  $R_7SO_4$ ; and  $s$  is the reciprocal of the number of negative charges in  $X$ ; and  $q$  and  $q'$  ranges from 0.01 to 1, wherein the polymer includes from 1 to 100% of a quaternized form of monomer; and 0.1-0.8% by weight of the polymer of a crosslinking agent.

The powdery quaternized polymers of the invention thus comprise:

(a) a strongly swellable, moderately crosslinked vinyl lactam, such as vinyl pyrrolidone (VP) or vinyl caprolactam (VC); with 0.1-0.8% of a crosslinking agent therein;

(b) an amino alkyl acrylamide or acrylate, such as dimethylaminopropyl methacrylamide (DMPMA) or dimethylaminoethyl methacrylate (DMAEMA); and, optionally,

(c) a polymerizable carboxylic acid, such as acrylic acid (AA) or methacrylic acid (MMA).

The powdery cationic polymers of the invention are made by precipitation polymerization in a non-aqueous solvent, particularly, a non-polar organic solvent cyclic or acyclic aliphatic hydrocarbon such as heptane or cyclohexane, an aromatic solvent such as benzene or toluene, an ether such as methyl tertiary butyl ether, or a ketone, such as acetone or methyl ethyl ketone. Both the polymer formation and quaternization steps are carried out in a heterogeneous medium in a non-polar solvent.

- 3 -

These powdery quaternized polymers find particular application as cationic thickening agents in cosmetic preparations, such as shampoo and hair conditioner products, and as controlled release or bioadhesive agents.

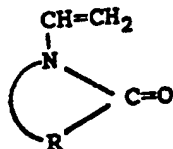
The powdery cationic polymers may be prepared by the steps of:

(1) precipitation polymerization in a non-polar organic solvent of (a) a vinyl lactam, (b) an amino alkyl acrylamide or acrylate, and, optionally, (c) a polymerizable carboxylic acid; with 0.1-0.8% by weight of a crosslinking agent,

(2) quaternization with a quaternizing agent, such as an alkyl halide, a dialkyl sulfate, chloroacetic acid, p-propiolactone, or chloromethyl pyrrolidone; and

(3) recovering the powdery quaternized polymer product.

Suitable vinyl lactam monomers for use herein have the formula:



where R is as defined above.

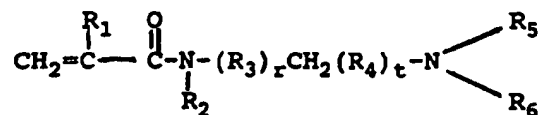
- 4 -

Representative vinyl lactams include:

N-vinyl pyrrolidone  
 N-vinyl caprolactam  
 N-vinyl piperidone  
 4-methyl-N-vinyl pyrrolidone  
 3,5-dimethyl-N-vinyl caprolactam  
 N-vinyl-hexahydro-2-azepinone  
 N-vinyl-octahydro-2-azocinone  
 N-vinyl octahydro-2-azoninone and  
 N-vinyl decahydro-2-azecinone.

Of these, N-vinyl pyrrolidone, N-vinyl caprolactam and the ring substituted alkyl derivatives of the N-vinyl caprolactam and N-vinyl pyrrolidone monomers are preferred. N-vinyl-2-pyrrolidone is most preferred.

Suitable amino alkyl acrylamide monomers useful in preparing the terpolymers of the present invention include amino alkyl acrylamides and methacrylamides of the general formula:



where  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ ,  $r$ ,  $\text{R}_4$ ,  $t$ ,  $\text{R}_5$  and  $\text{R}_6$  are as defined above.

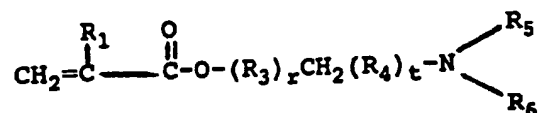
Examples of amino alkyl acrylamides which are employed as monomers herein include:

N-[3-(dimethylamino) propyl]methacrylamide (DMAPMA)  
 N-[12-(dimethylamino) dodecyl]methacrylamide  
 N-[18-(dimethylamino) octadecyl]methacrylamide  
 N-[8-(dimethylamino) octyl]methacrylamide

- 5 -

N-[7-(dimethylamino) heptyl]acrylamide  
 N-[14-(dimethylamino) tetradecyl]acrylamide  
 N-[3-(dimethylamino) propyl]methacrylamide  
 N-[3-(diethylamino) propyl]acrylamide  
 N-(4-(dipropylamino) butyl]methacrylamide  
 N-[3-(methyl butyl amino) propyl]acrylamide  
 N-(2-[3-(dimethylamino) propyl] ethyl]acrylamide  
 N-(4-[4-(diethylamino) butyl]butyl)acrylamide.

Amino alkyl acrylate monomers useful in preparing the terpolymers of the invention have the formula:



where  $\text{R}_1$ ,  $\text{R}_3$ ,  $r$ ,  $\text{R}_4$ ,  $t$ ,  $\text{R}_5$  and  $\text{R}_6$  are as defined above.

Exemplary amino alkyl acrylates or methacrylates suitably employed in the production of the terpolymers of the present invention include:

dimethylaminomethyl acrylate  
 dimethylaminomethyl methacrylate  
 diethylaminomethyl acrylate  
 diethylaminomethyl methacrylate  
 dimethylaminoethyl acrylate  
 dimethylaminoethyl methacrylate (DMAEMA)  
 dimethylaminobutyl acrylate  
 dimethylaminobutyl methacrylate  
 dimethylaminoamyl methacrylate  
 diethylaminoamyl methacrylate

- 6 -

dimethylaminohexyl acrylate  
diethylaminohexyl methacrylate  
dimethylaminooctyl acrylate  
dimethylaminooctyl methacrylate  
diethylaminooctyl acrylate  
diethylaminooctyl methacrylate  
dimethylaminodecyl methacrylate  
dimethylaminododecyl methacrylate  
diethylaminolauryl acrylate  
diethylaminolauryl methacrylate  
dimethylaminostearyl acrylate  
dimethylaminostearyl methacrylate  
diethylaminostearyl acrylate  
diethylaminostearyl methacrylate.

Suitable polymerizable carboxylic acid monomers  
for use herein include:

acrylic acid  
methacrylic acid  
maleic acid  
itaconic acid  
3-phenyl-2-propenic acid  
crotonic acid and  
fumaric acid.



Suitable crosslinking agents for use in the invention include such multifunctional compounds as the divinyl ethers of an aliphatic diol, e.g. the divinyl ethers of 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-unidecanediol, and 1,12-dodecanediol; as well as the divinyl ethers of diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, heptaethylene glycol, octaethylene glycol, nonaethylene glycol, decaethylene glycol and further polyalkylene glycols up to a molecular weight of about 6000. Other suitable crosslinking agents include 1,7-octadiene, 1,9-decadiene, 1,13-tetradecadiene, divinylbenzene, N,N'-divinylimidazolidone, and methylene bisacrylamide; acrylates such as polyethylene glycol diacrylate, trimethylolpropane triacrylate, propylene glycol diacrylate; allyl ether derivatives of polyhydric alcohols such as pentaerythritol triallyl ether; or polyhydric alcohols esterified once or twice with acrylic acid; triallylamine, tetraallylethylene diamine, diallyl phthalate, and the like. Preferred crosslinking agents are the following: N,N'-divinylimidazolidone, pentaerythritol triallyl ether, triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione and 2,4,6-triallyloxy-1,3,5-triazine.

The powdery quaternized polymers of the present invention are conveniently prepared by subjecting a solution of (a) the vinyl lactam, preferably vinyl pyrrolidone, (b) the amino alkyl acrylamide or acrylate monomer, optionally, (c) and the polymerizable carboxylic acid monomer, preferably acrylic acid, and (d) crosslinking agent to conditions conducive to polymerization through double bonds. Thus, for example,

- 8 -

the reaction can be suitably initiated by the action of free radicals, polymerization proceeding exothermically once initiated. Suitable free radical initiators conveniently employed and suitably utilized in accordance with the production of the copolymers of the present invention include organic and inorganic peroxide and perester compounds e.g., hydrogen peroxide, lauryl peroxide, decanoyl peroxide, di-tert-butyl peroxide, tert-butyl peroxyvalate, etc., aliphatic azo compounds, e.g., azobisisobutyronitrile, as well as other free radical initiators well known in the polymerization art.

The polymerization reaction of the present invention takes place in the presence of a solvent. In this invention, precipitation polymerization is employed to provide the quaternized polymer in powder form. Suitable solvents for this use are non-polar organic solvents, preferably cyclic or acyclic, such as aliphatic hydrocarbons, such as hexane, heptane and cyclohexane. Heptane and cyclohexane are preferred. Both the formation of the polymer and the quaternization of the powdery polymer to form a powdery quaternized polymer, are carried out heterogeneously.

The precipitation polymerization reaction is effected at a temperature between about 40°C. and about 130°C. under from about 14 to about 50 psia. for a period of from about 1 to about 20 hours. To avoid run away conditions and to obtain a polymer of a desirable high molecular weight it is preferred to carry out the polymerization at the lower end of the temperature range, e.g. between about 50°C. and about 80°C. The polymerization reaction is preferably carried out in the absence of free oxygen, conveniently under a blanket of an inert gas, such as nitrogen, argon or the like, and at atmospheric pressure.

The polymers of the invention can be made by precipitation polymerization within the complete compositional range of monomer components. Accordingly, the polymers can be formed from 1-99% by weight of each of the monomer components; preferably (a) 50 to 90%; (b) 10 to 50%; and (c) 0-15%.

In the preparation of the powdery quaternized polymers of the present invention, it is only necessary to mix the monomers in the ratios set forth above in order to provide a polymer product produced through vinyl polymerization initiated by the action of free radicals. Generally, the polymer is produced within a period of a few hours, e.g. less than about 10 hours. The feeding rates of the VP and DMAPMA monomers, for example, which may be added separately or in admixture, suitably is about 0.1 ml/min/kg solvent to 1.0 ml/min/kg solvent, preferably 0.4-0.7 ml/min/kg solvent; and the polymerizable carboxylic acid and crosslinking agent are added during the same period of time.

The present cationic polymeric products are particularly useful as viscosity builders for cosmetic creams and lotions as well as for such hair treatment compositions to provide body and retentative moisturizing. When incorporated into standard formulations such as hair sprays, hair setting lotions, shampoos, hair and skin conditioners, and other personal care products, the amount of polymeric product used can range between about 0.05 weight % and about 8 weight %, based on total formulation. Usually not more than 4% is required to achieve the above desirable affects. The present powdery quaternized polymer or polymer mixture may be conveniently added to the cosmetic formulations as the powder itself, or as an aqueous or non-aqueous solution containing from about 1% to about 10% of polymer.

**BEST AVAILABLE COPY**

- 10 -

EXAMPLE

In a 2-liter, four-necked reaction kettle (bottom radius = 5 and 1/8 inches) equipped with a condenser, a constant speed (set at 170 rpm) mechanical stirrer with torque reading and anchor agitator (open radius = 4 and 5/6 inches), a dip tube connected to metering pump, a nitrogen purge adaptor, and a thermocouple connected to the temperature controller, 1000 grams of heptane were charged and the reactor was heated to 65°C. in 30 minutes with nitrogen purge throughout the whole process. Hold the reactor at 65°C. in 30 minutes. Add 520 microliters of t-butylperoxypivalate (Lupersol 11) into the reactor and feed the solution of VP, DMAPMAA and desired amount of crosslinking agent into reactor at a rate of 0.60 ml/min. A total of 2 g. of acrylic acid then was added in equal amounts every 15 minutes for 6 hours. After VP and DMAPMAA were fed completely, the mixture was kept stirring at 65°C. for overnight. Then, the reactor was heated to 85°C., over half hour and held another half hour. Charged 200 microliters of t-butylperoxypivalate at every hour for 4 hours at 85°C. Cooled the reactor to 40°C. and added 18.12 grams of diethyl sulfate to completely quaternize the DMAPMAA. The reaction was run for 4 hours at 40°C. and was cooled to room temperature and the mixture was poured into a pan. The polymer was dried in the oven (100°C.), and vacuum oven (90°C.) for 16 hours each.

BEST AVAILABLE COPY

### Properties of Polymer of Invention

The strongly swellable, moderately crosslinked polymer powders of the invention in suitable aqueous or non-aqueous solution are characterized by its unique gel volume and viscosity, which properties enable the polymer to thicken aqueous and non-aqueous solutions effectively.

Gel volume is a measure of the swelling property of the crosslinked polymer and is defined as the equilibrium aqueous swelling volume of polymer per unit weight, and is expressed in the units of ml/g. Gel volume is determined by first adding 1 g. of the polymer to a suitable graduated cylinder filled with water. This mixture then is shaken and allowed to stand at room temperature for 3 days. The volume of the gel which is produced in water is measured and taken as the gel volume. Similarly, the gel volume concept can be applied to non-aqueous systems.

The viscosity of the polymer is defined by its Brookfield viscosity in cps, which is determined upon a 4% aqueous solution of the polymer at 25°C. by a standard analytical procedure using Model RTV and Spindle No. 4.

Figure 1 is a graphical representation of Brookfield viscosity and gel volume vs. at a concentration of 4% by weight crosslinker for an aqueous cationic polymer composition of a cationic polymer composition of 79 weight % of strongly swellable, moderately crosslinked vinylpyrrolidone (VP) crosslinked with triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATT), and 19 weight % of quaternized dimethylaminopropyl methacrylamide (DMAPMAA), and 2 weight % acrylic acid, at a 4% by weight level.

Figure 2 is a graphical representation of Brookfield viscosity vs. aqueous concentration for the cationic polymer composition of Figure 1 at a 0.45% TATT level.

- 12 -

Referring now to Figure 1, there is shown the Brookfield viscosity and gel volume parameters vs. % crosslinker for an aqueous solution of the cationic polymers of the invention. For maximum utility, it is desirable that the hydrated polymer exhibit a high gel volume and a high viscosity. With increasing crosslinking density in the polymer, the gel volume decreases and viscosity increases and then decreases, passing through a maximum. In the crosslinked polymer system of this invention, an effective thickener product is provided by including crosslinker in the reaction mixture at a suitable concentration of about 0.1 to 0.8% by weight, based upon VP, preferably about 0.2 to 0.6%. At this suitable amount of crosslinker loading, the crosslinked polymer product exhibits a gel volume of about 50 to 150 ml/g of polymer and a Brookfield viscosity of at least 10,000 cps. At the preferred crosslinker concentration, the gel volume is about 70 to 90 ml/g of polymer and its Brookfield viscosity is at least 23,000 cps. At the optimal amount crosslinker present in the reaction mixture of 0.25%, the polymer exhibits a gel volume of about 85 ml/g of polymer and a Brookfield viscosity of about 57,000 cps.

Figure 2 shows the effect of polymer concentration in aqueous solution upon Brookfield viscosity at a 0.45% crosslinker level. Suitably, the polymer concentration is 1-10% by weight of the solution preferably about 2-8%. The viscosity increases dramatically above 4%.

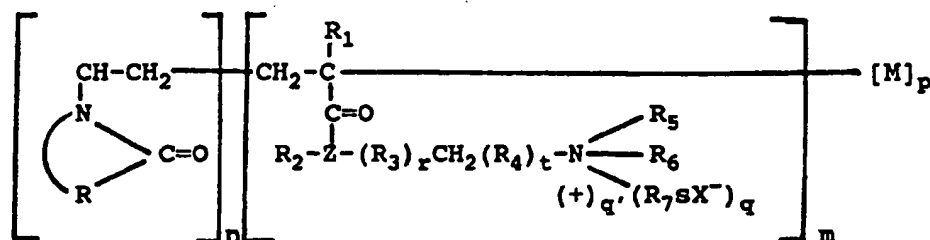
As an added feature of the invention, the residual VP monomer content of the polymers obtained herein is less than about 0.1% by weight. In aqueous based processes, in contrast, the formation of a gel mass during polymerization may trap considerable amounts of VP monomer in the polymeric gel network.

- 13 -

## WHAT IS CLAIMED IS:

1. A cationic polymer comprising (a) a strongly swellable, moderately crosslinked vinyl lactam including (b) about 0.1-0.8% by weight of a crosslinking agent, (c) a quaternized amino alkyl acrylamide or acrylate, and, (d) optionally, a polymerizable carboxylic acid.

2. Polymers according to claim 1 represented by the formula:

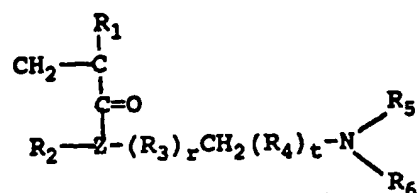


where R is alkylene having from 3 to 8 carbon atoms; R<sub>1</sub> and R<sub>2</sub> are each independently hydrogen or methyl; R<sub>3</sub> and R<sub>4</sub> are each alkylene having from 1 to 18 carbon atoms optionally substituted with alkyl; the sum of r and t is one or zero; R<sub>5</sub> and R<sub>6</sub> are each independently lower alkyl; Z is oxygen or nitrogen; if oxygen, R<sub>2</sub> is absent; M is a polymerizable carboxylic acid; n has a value of from 1 to 99 mole %; m has a value of from 1 to 99 mole %; p has a value of from 0 to 98 mole %; the sum of m + n + p is 100 mole %; preferably n is 50 to 90 mole %; m is 7 to 25 mole % and p 3 to 25 mole %; R<sub>7</sub>SX<sup>-</sup> is a quaternizing group, in which R<sub>7</sub> is lower alkyl, pyrrolidonyl alkyl, carboxymethylene, or a zwitterion of  $\beta$ -propiolactone; X is an anion derived from the group of halogen, SO<sub>3</sub>, SO<sub>4</sub>, HSO<sub>4</sub> and R<sub>7</sub>SO<sub>4</sub>; and s is the reciprocal of the number of negative charges in X; and q and q' ranges from 0.01 to 1, wherein the polymer includes from 1 to 100% of a quaternized form of monomer.

- 14 -

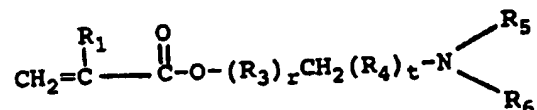
3. The polymer of claim 2 wherein R is alkylene having 3 to 5 carbon atoms.

4. The polymer of claim 2 wherein the amino alkyl acrylamide moiety has the formula:



wherein  $R_1$ ,  $R_2$ ,  $R_3$ ,  $r$ ,  $R_4$ ,  $t$ ,  $R_5$  and  $R_6$  are as defined in claim 2.

5. The polymer of claim 2 wherein the amino alkyl acrylate moiety has the formula



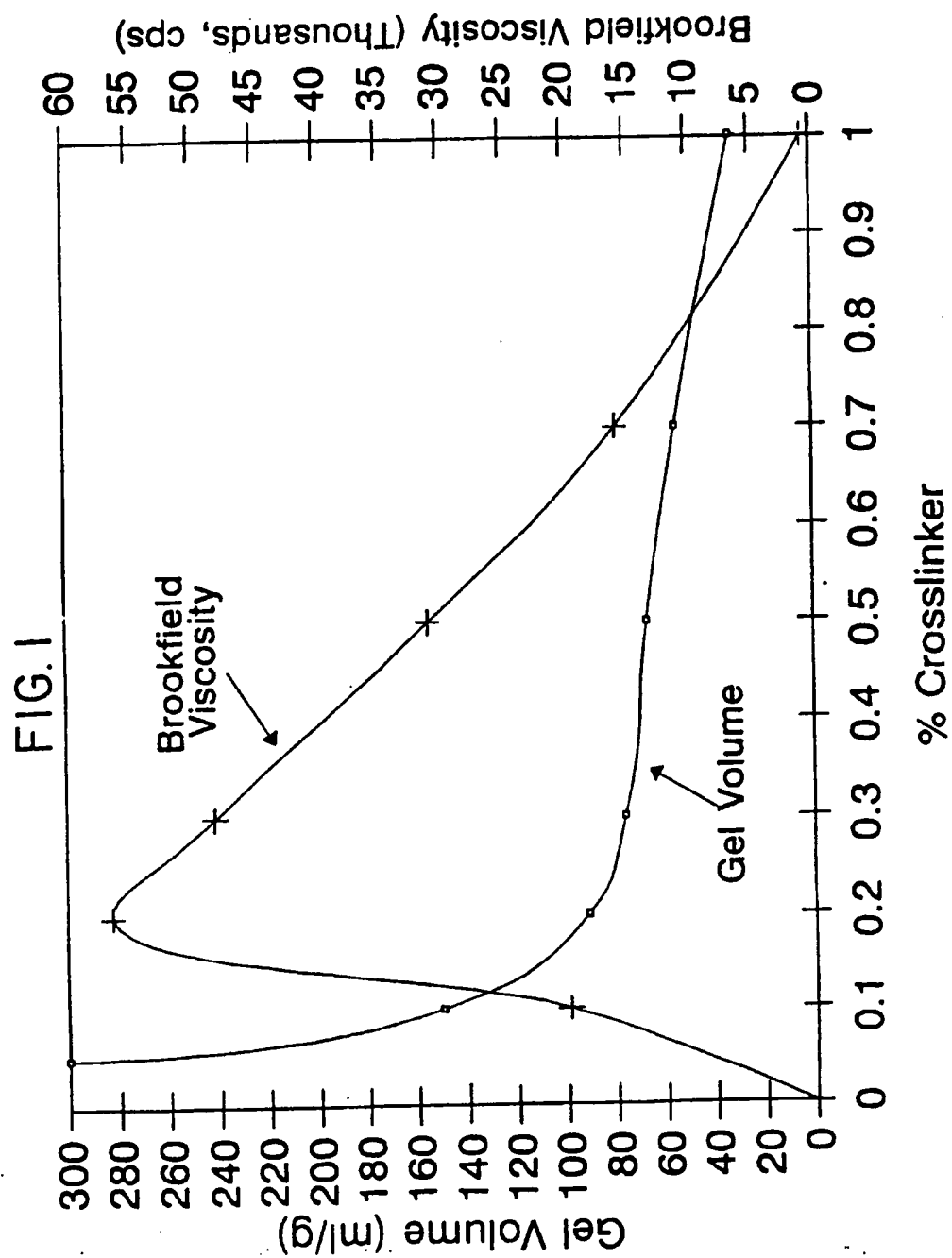
where  $R_1$ ,  $R_3$ ,  $r$ ,  $R_4$ ,  $t$ ,  $R_5$  and  $R_6$  are as defined in claim 2.

6. The polymer of claim 2 wherein the polymerizable carboxylic acid group is derived from the group selected from acrylic acid, methacrylic acid, maleic acid, crotonic acid, 3-phenyl-2-propenic acid, fumaric acid and itaconic acid.

7. The polymer of claim 2 wherein  $n$  is 50 to 90 mole %;  $m$  is 7 to 25 mole %; and  $p$  is 1 to 25 mole %.

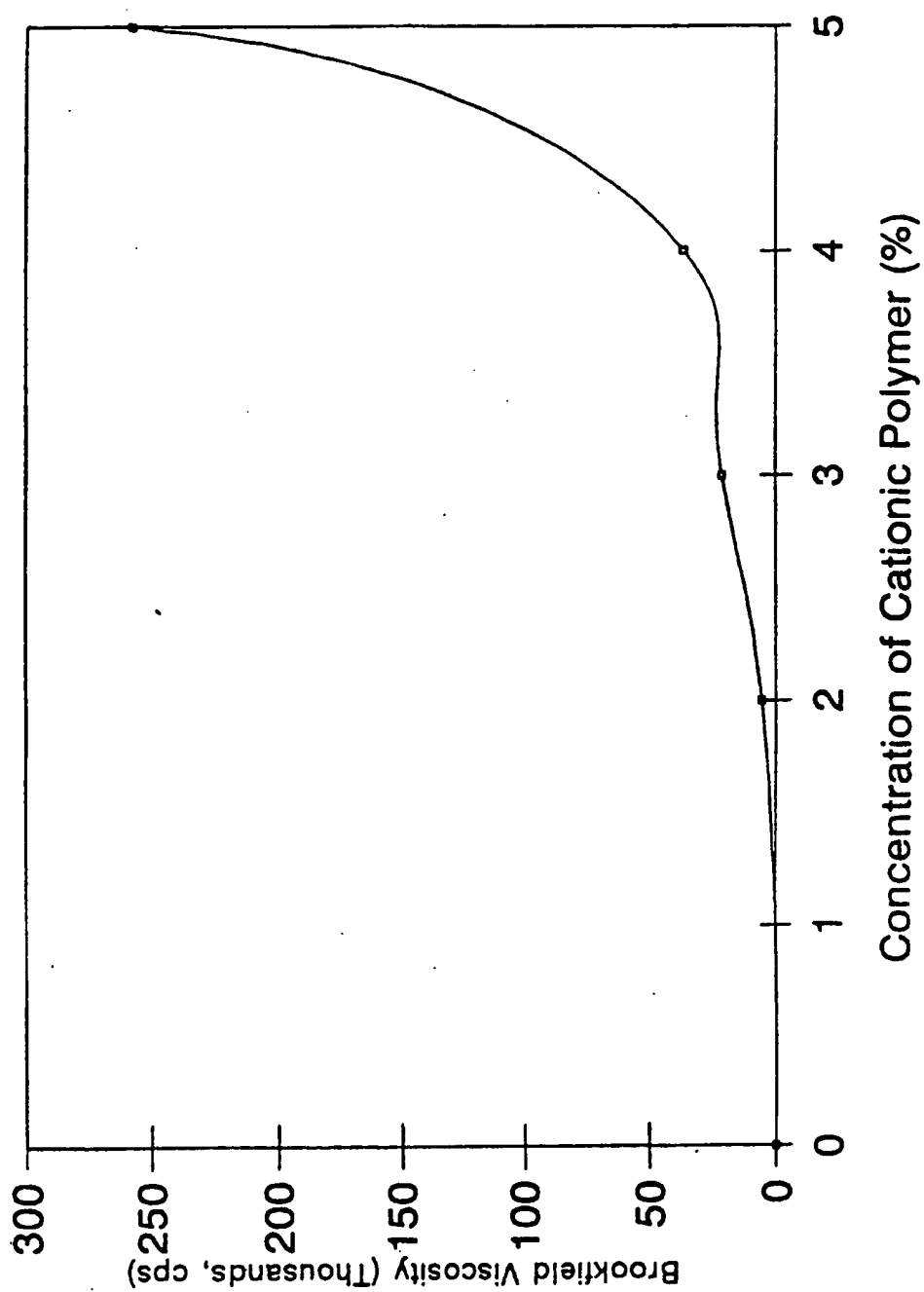


1 / 2



2 / 2

FIG. 2



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/04823

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(5) : C08F 226/06, 220/60, 220/04, 220/34 US CL : 526/264, 307, 317.1, 328.5 According to International Patent Classification (IPC) or to both national classification and IPC																								
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 526/264, 307, 317.1, 328.5  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)																								
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>																								
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																						
Y	US, A, 3,910,862 (BARABAS et al) 07 OCTOBER 1975, see the abstract.	1-7																						
Y	US, A, 3,933,766 (HOFMANN et al) 20 JANUARY 1976, see column 2, lines 43-52.	1-7																						
Y,P	US, A, 5,153,289 (SCHULZ et al) 06 OCTOBER 1992, see the abstract.	1-5																						
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.																								
<table border="0"><tr><td>* Special categories of cited documents:</td><td>*T</td><td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td></tr><tr><td>*A</td><td>document defining the general state of the art which is not considered to be part of particular relevance</td><td></td></tr><tr><td>*E</td><td>earlier document published on or after the international filing date</td><td>*X</td><td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td></tr><tr><td>*L</td><td>document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td><td>*Y</td><td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td></tr><tr><td>*O</td><td>document referring to an oral disclosure, use, exhibition or other means</td><td>*Z</td><td>document member of the same patent family</td></tr><tr><td>*P</td><td>document published prior to the international filing date but later than the priority date claimed</td><td></td><td></td></tr></table>			* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	*A	document defining the general state of the art which is not considered to be part of particular relevance		*E	earlier document published on or after the international filing date	*X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	*L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	*O	document referring to an oral disclosure, use, exhibition or other means	*Z	document member of the same patent family	*P	document published prior to the international filing date but later than the priority date claimed		
* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention																						
*A	document defining the general state of the art which is not considered to be part of particular relevance																							
*E	earlier document published on or after the international filing date	*X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																					
*L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																					
*O	document referring to an oral disclosure, use, exhibition or other means	*Z	document member of the same patent family																					
*P	document published prior to the international filing date but later than the priority date claimed																							
Date of the actual completion of the international search 29 JUNE 1993		Date of mailing of the international search report 02 AUG 1993																						
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No.: NOT APPLICABLE		Authorized officer W.C. CHENG Telephone No. (703) 308-2351																						